A. Acidity of Carboxylic and Sulfonic Acids

The acidity of carboxylic acids is one of their most important chemical properties. This acidity is due to ionization of the O—H group.

\[
\begin{align*}
\text{carboxylic acid} & \quad \text{+ H}_2\text{O} \quad \rightarrow \quad \text{carboxylate ion} \\
\end{align*}
\]

The conjugate bases of carboxylic acids are called generally carboxylate ions. Carboxylate salts are named by replacing the \textit{ic} in the name of the acid (in any system of nomenclature) with the suffix \textit{ate}.

Carboxylic acids are among the most acidic organic compounds; acetic acid, for example, has a p\(K_a\) of 4.76. This p\(K_a\) is low enough that an aqueous solution of acetic acid gives an acid reaction with litmus or pH paper.

Carboxylic acids are more acidic than alcohols or phenols, other compounds with O—H bonds.

The acidity of carboxylic acids is due to two factors. First is the polar effect of the carbonyl group. The carbonyl group, because of its \(sp^2\)-hybridized atoms, the partial positive charge on the carbonyl carbon, and the presence of oxygen, is a very electronegative group, much more electronegative than the phenyl ring of a phenol or the alkyl group of an alcohol. The polar effect of the carbonyl group stabilizes charge in the carboxylate ion. Remember that stabilization of a conjugate base enhances acidity (Fig. 3.2, p. 113).

The second factor that accounts for the acidity of carboxylic acids is the resonance stabilization of their conjugate-base carboxylate ions.
Although typical carboxylic acids have $pK_a$ values in the 4–5 range, the acidities of carboxylic acids vary with structure. Recall, for example (Sec. 3.6C), that halogen substitution within the alkyl group of a carboxylic acid enhances acidity by a polar effect.

Trifluoroacetic acid, commonly abbreviated TFA, is such a strong acid that it is often used in place of HCl and $H_2SO_4$ when an acid of moderate strength is required.

The $pK_a$ values of some carboxylic acids are given in Table 20.2, and the $pK_a$ values of the simple dicarboxylic acids in Table 20.3. The data in these tables give some idea of the range over which the acidities of carboxylic acids vary.

Sulfonic acids are much stronger than comparably substituted carboxylic acids.

One reason that sulfonic acids are more acidic than carboxylic acids is the high oxidation state of sulfur. The octet structure for a sulfonate anion indicates that sulfur has considerable positive charge. This positive charge stabilizes the negative charge on the oxygens.

### Table 20.2: $pK_a$ Values of Some Carboxylic Acids

<table>
<thead>
<tr>
<th>Acid*</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>formic</td>
<td>3.75</td>
</tr>
<tr>
<td>acetic</td>
<td>4.76</td>
</tr>
<tr>
<td>propionic</td>
<td>4.87</td>
</tr>
<tr>
<td>2,2-dimethylpropanoic (pivalic)</td>
<td>5.05</td>
</tr>
<tr>
<td>acrylic</td>
<td>4.26</td>
</tr>
<tr>
<td>chloroacetic</td>
<td>2.85</td>
</tr>
<tr>
<td>phenylacetic</td>
<td>4.31</td>
</tr>
<tr>
<td>benzoic</td>
<td>4.18</td>
</tr>
<tr>
<td>$p$-methylbenzoic ($p$-toluic)</td>
<td>4.37</td>
</tr>
<tr>
<td>$p$-nitrobenzoic</td>
<td>3.43</td>
</tr>
<tr>
<td>$p$-chlorobenzoic</td>
<td>3.98</td>
</tr>
<tr>
<td>$p$-methoxybenzoic ($p$-anisic)</td>
<td>4.47</td>
</tr>
<tr>
<td>2,4,6-trinitrobenzoic</td>
<td>0.65</td>
</tr>
</tbody>
</table>

*See Table 20.1 for structures.

### Table 20.3: $pK_a$ Values of Some Dicarboxylic Acids

<table>
<thead>
<tr>
<th>Acid*</th>
<th>First $pK_a$</th>
<th>Second $pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbonic</td>
<td>3.77</td>
<td>10.33</td>
</tr>
<tr>
<td>oxalic</td>
<td>1.27</td>
<td>4.27</td>
</tr>
<tr>
<td>malonic</td>
<td>2.86</td>
<td>5.70</td>
</tr>
<tr>
<td>succinonic</td>
<td>4.21</td>
<td>5.64</td>
</tr>
<tr>
<td>glutaric</td>
<td>4.34</td>
<td>5.27</td>
</tr>
<tr>
<td>adipic</td>
<td>4.41</td>
<td>5.28</td>
</tr>
<tr>
<td>phthalic</td>
<td>2.95</td>
<td>5.41</td>
</tr>
</tbody>
</table>

*See Table 20.1 for structures.

*This value, which corrects for the amount of $H_2CO_3$ in aqueous CO$_2$, is the actual $pK_a$ of carbonic acid. An often-cited value of 6.4 treats all dissolved CO$_2$ as $H_2CO_3$. 

$$\text{H}_3\text{C}—\text{CO}_2\text{H}\quad \text{FCH}_2—\text{CO}_2\text{H}\quad \text{F}_2\text{CH}—\text{CO}_2\text{H}\quad \text{F}_3\text{C}—\text{CO}_2\text{H} \quad (20.5)$$

$\text{acetic acid} \quad \text{fluoroacetic acid} \quad \text{difluoroacetic acid} \quad \text{trifluoroacetic acid}$

$$\text{p}_K\text{a} \quad 4.76 \quad 2.66 \quad 1.24 \quad 0.23$$

Trifluoroacetic acid, commonly abbreviated TFA, is such a strong acid that it is often used in place of HCl and $H_2SO_4$ when an acid of moderate strength is required.
Sulfonic acids are useful as acid catalysts in organic solvents because they are more soluble than most inorganic acids. For example, \( p \)-toluenesulfonic acid is moderately soluble in benzene and toluene and can be used as a strong acid catalyst in those solvents. (Sulfuric acid, in contrast, is completely insoluble in benzene and toluene.)

Many carboxylic acids of moderate molecular mass are insoluble in water. Their alkali metal salts, however, are ionic compounds, and in many cases are much more soluble in water. Therefore many water-insoluble carboxylic acids dissolve in solutions of alkali metal hydroxides (\( \text{NaOH}, \text{KOH} \)) because the insoluble acids are converted completely into their soluble salts.

Even a 5% sodium bicarbonate (\( \text{NaHCO}_3 \)) solution is basic enough (pH \( \approx 8.5 \)) to dissolve a carboxylic acid. This can be understood from the equilibrium expression for the ionization of a carboxylic acid \( \text{RCO}_2\text{H} \) with a dissociation constant \( K_a \).

\[
K_a = \frac{[\text{RCO}_2^-][\text{H}_3\text{O}^+]}{[\text{RCO}_2\text{H}]} \tag{20.7a}
\]

or

\[
\frac{K_a}{[\text{H}_3\text{O}^+]} = \frac{[\text{RCO}_2^-]}{[\text{RCO}_2\text{H}]} \tag{20.7b}
\]

For the carboxylic acid to dissolve in water, it must be mostly ionized and in its soluble conjugate-base form \( \text{RCO}_2^- \); that is, in Eq. 20.7b, the ratio \( [\text{RCO}_2^-]/[\text{RCO}_2\text{H}] \) has to be large. As a practical matter, we can say that when this ratio is 100 or greater, the acid has been completely converted into its anion. (There is no pH at which the acid exists completely as its anion; but when this ratio is \( \approx 100 \), the concentration of acid is negligible.) Because \( K_a \) is a constant, Eq. 20.7b shows that this ratio can be made large by making the hydrogen-ion concentration \( [\text{H}_3\text{O}^+] \) small in comparison with the \( K_a \) of the acid. Taking negative logarithms of Eq. 20.7b gives the following result:

\[
\text{pH} - \text{p}K_a = \log \frac{[\text{RCO}_2^-]}{[\text{RCO}_2\text{H}]} \tag{20.7c}
\]

(This logarithmic form of the dissociation equation is sometimes known as the Henderson–Hasselbalch equation.) If \( [\text{RCO}_2^-]/[\text{RCO}_2\text{H}] \) is \( \approx 100 \), then the logarithm of this ratio is \( \approx 2 \). Equation 20.7c shows that, for the conversion of an acid into its anion, the pH of the solution must be two or more units greater than the p\( K_a \) of the acid. Because the pH of a 5% sodium bicarbonate solution is about 8.5, and most carboxylic acids have p\( K_a \) values in the range 4–5, sodium bicarbonate solution is more than basic enough to dissolve a typical acid, provided that enough bicarbonate is present that it is not completely consumed by its reaction with the acid.

A typical carboxylic acid, then, can be separated from mixtures with other water-insoluble, nonacidic substances by extraction with NaOH, \( \text{Na}_2\text{CO}_3 \), or \( \text{NaHCO}_3 \) solution. The acid dis-
solves in the basic aqueous solution, but nonacidic compounds do not. After separating the basic aqueous solution, it can be acidified with a strong acid to yield the carboxylic acid, which may be isolated by filtration or extraction with organic solvents. (A similar idea was used in the separation of phenols; Sec. 18.7B.) Carboxylic acids can also be separated from phenols by extraction with 5% NaHCO₃ if the phenol is not unusually acidic. Because the pKₐ of a typical phenol is about 10, it remains largely un-ionized and thus insoluble in an aqueous solution with a pH of 8.5. (This conclusion follows from an equation for phenol ionization analogous to Eq. 20.7c.)

**B. Basicity of Carboxylic Acids**

Although we think of carboxylic acids primarily as acids, the carbonyl oxygens of acids, like those of aldehydes or ketones, are weakly basic.

\[
\begin{align*}
\text{R} & \quad \text{C} \quad \text{O} \quad \text{H} + \text{H}_3\text{O}^+ \\
\text{R} & \quad \text{C} \quad \text{O} \quad \text{H} + \text{H}_2\text{O} & \text{protonated carboxylic acid} \quad \text{pK}_a = -6
\end{align*}
\]

(20.8)

The basicity of carboxylic acids plays a very important role in many of their reactions. Protonation of an acid on the *carbonyl oxygen* occurs because, as Eq. 20.8 shows, a resonance-stabilized cation is formed. Protonation on the *carboxylate oxygen* is much less favorable because it does not give a resonance-stabilized cation and because the positive charge on oxygen is destabilized by the polar effect of the carbonyl group.

\[
\begin{align*}
\text{R} & \quad \text{C} \quad \text{O} \quad \text{H} \\
\text{R} & \quad \text{C} \quad \text{O} \quad \text{H} \\
\text{resonance-stabilized} \quad \text{(Eq. 20.8)} & \quad \text{not resonance-stabilized; does not form}
\end{align*}
\]

**20.5 FATTY ACIDS, SOAPS, AND DETERGENTS**

Carboxylic acids with long, unbranched carbon chains are called **fatty acids** because many of them are liberated from fats and oils by a hydrolytic process called *saponification* (Sec. 21.7A). Some fatty acids contain carbon–carbon double bonds. Fatty acids with cis double bonds occur...